

Progress Report

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Photolysis of Nitric Oxide and Carbon Dioxide

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Nitric Oxide.

In the nitric oxide study, by using high flow rates it has been possible to demonstrate the production of nitrous oxide during photolysis at 1470A whereas in the static system only negligible traces, if any, were found. It has, therefore, been possible to assess the quantum yield of nitrous oxide production in the flow system in addition to the yields of nitrogen and nitrogen dioxide. Since the extent of photolysis of nitric oxide at these fast flow rates is small, the precision of any determination of the quantum yield of disappearance of nitric oxide, since it involves a small difference of two large values, is necessarily unreliable.

Considerable difficulty was experienced, in these fast flow photolyses, to achieve consistency and reproducibility. In part, this was probably due to some turbulence in the flow and it became necessary to use an average exposure time calculated from the total flow, the volume of the reactor and the duration of the experiment. These values proved to be consistent and reasonably reproducible.

A second difficulty encountered lay in the presence of small quantities of nitrogen and nitrous oxide in the nitric oxide being used. Whereas these were only traces in the earlier static runs, their accumulation in the dynamic system necessitated their precise assessment in the product analysis of the now relatively large volume of gas and allowance had to be made for the amounts present in the intake gas. It is this allowance, for the volumes involved that is unprecise. A purification of tank nitric oxide in the laboratory using low-temperature fractionation though possible is hardly feasible for the relatively large quantities of gas needed. The Precision Gas Co. of New Jersey agreed to supply small Lecture bottles of nitric oxide of 99.99 per cent purity and the traces of nitrogen and nitrous oxide, demonstrated by mass-spectrograms and gas-chromatograms could be allowed for satisfactorily in the product analysis.

The effect which the surmounting of these problems made in the overall picture can be judged by a comparison of the data in Table I, which were obtained using the slightly impure nitric oxide and attemptedly allowing for the amount of impurity relative to the product amount, with the data in Table II, using the pure nitric oxide. The data are illustrative but do not cover all runs made. The inconsistencies in Table I

are apparent. Comparison of runs 10 and 18 made with almost the same flow rate shows no agreement in the calculated quantum yields. By contrast, the data in Table II are completely consistent and plots of the data give smooth curves showing, initially, a steady increase in quantum yield with exposure time, levelling off to a limiting values. Further runs are needed to fix these limiting values which are important in the confirmation of mechanism.

Table I

Run	Moles/min NO x 10 ⁵	Quantum Yields		
		N ₂	N ₂ O	NO ₂
19	13.49	2.53	0.47	0.14
15	9.51	0.39	1.38	0.13
10	8.11	0.81	6.7	0.43
18	8.01	1.8	3.95	-
17	6.61	1.1	0.20	0.06
13	3.65	0.44	0.16	0.18
16	1.99	0.74	0.16	0.12

Table II

Run	Moles/min NO x 10 ⁵	Exposure time	Quantum Yields		
			N ₂	N ₂ O	NO ₂
54	23.95	1.12	0.62	0.22	0.08
55	16.93	1.24	0.83	0.25	0.12
53	10.42	1.97	0.57	0.17	0.05
51	6.93	2.43	0.42	0.13	0.02
56	0.62	5.67	0.09	0.039	0.044
52	0.14	19.08	0.07	0.06	0.06

Carbon dioxide.

The apparatus for the carbon dioxide photolysis study involves the incorporation in the reaction vessel of a quartz spring balance and a thermal conductivity gauge. The former requires, by preliminary survey, finding the best adsorbent for the oxygen atoms produced in the photolysis of carbon dioxide, an adsorbent which must not appreciably absorb carbon dioxide, or, if it does, does so only slowly, and a critical assessment of the sensitivity of the quartz spiral balance. Work is in progress along these lines and data have been obtained for silver oxide as adsorbent. The oxygen atom adsorption appears to be weak and a higher sensitivity of measurement than that of the current instrument may be required. Other oxides or perhaps metals will be tried. Once a satisfactory adsorbent is found, the actual photolysis data could be accumulated rapidly.